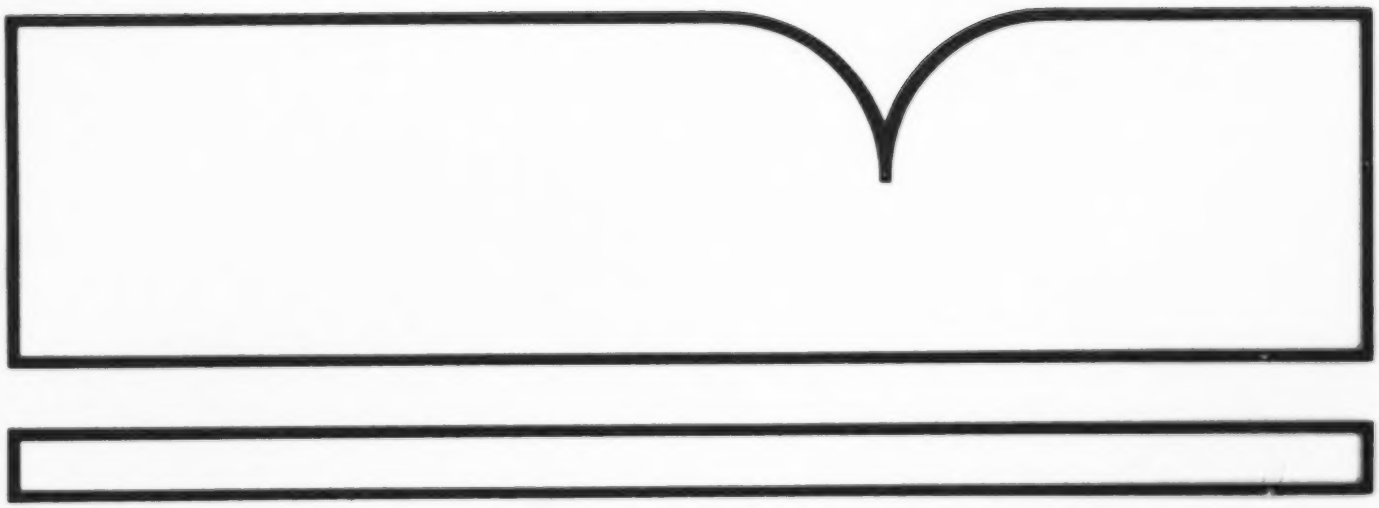
PB87-175048

Nitric Acid-Air Diffusion Coefficient Experimental Determination

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

1986



U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RE PB87-175048
EPA/600/J-86/289		

4. TITLE AND SUBTITLE
NITRIC ACID-AIR DIFFUSION COEFFICIENT: EXPERIMENTAL DETERMINATION (Journal Version)

5. REPORT DATE
1986

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
J. L. Durham and L. Stockburger

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Same as Box No. 12

10. PROGRAM ELEMENT NO.
CCVN1A/06 Task 2347 FY-85

11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS
Atmospheric Sciences Research Laboratory - RTP, NC
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

13. TYPE OF REPORT AND PERIOD COVERED

14. SPONSORING AGENCY CODE
EPA/600/09

15. SUPPLEMENTARY NOTES
Atmospheric Environment, 20(3):559-563, March 1986

16. ABSTRACT

Trace gaseous HNO_3 in air is removed in a laminar flow nylon tube. The HNO_3 deposition pattern was obtained by sectioning the tube, extracting with an aqueous solution, and measuring the concentration by ion chromatography. Mass transport analysis of the deposition pattern demonstrated the HNO_3 was removed from the air stream at a rate controlled by gaseous diffusion. The HNO_3-air diffusion coefficient = 0.116 ± 0.003 cm^2/s (n = 7) for t = 298 K and p = 1 atm. It exhibited no dependence on relative humidity over the range 5 - 95%.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	7
	20. SECURITY CLASS (This page)	22. PRICE
	UNCLASSIFIED	

EPA/600/J-86/289
JOURNAL ARTICLE

Atmospheric Environment Vol. 20, No. 3, pp. 559–563, 1986
Printed in Great Britain.

0004-6981/86 $3.00 + 0.00
Pergamon Press Ltd.

NITRIC ACID–AIR DIFFUSION COEFFICIENT: EXPERIMENTAL DETERMINATION

J. L. DURHAM and L. STOCKBURGER

Atmospheric Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, U.S.A.

(*First received* 8 *May* 1985 *and in final form* 29 *July* 1985)

Abstract—Trace gaseous HNO_3 in air is removed in a laminar flow nylon tube. The HNO_3 deposition pattern was obtained by sectioning the tube, extracting with an aqueous solution, and measuring the concentration by ion chromatography. Mass transport analysis of the deposition pattern demonstrated the HNO_3 was removed from the air stream at a rate controlled by gaseous diffusion. The HNO_3–air diffusion coefficient = $0.118 \pm 0.003\ cm^2\ s^{-1}$ ($n = 7$) for $T = 298$ K and $P = 1$ atm. It exhibited no dependence on relative humidity over the range 5–95%.

Key word index: Nitric acid, relative humidity, diffusion coefficient, denuder tube.

INTRODUCTION

The deposition of nitric acid (HNO_3) to the earth's surface has been associated with ecosystem acidification (Likens *et al.*, 1977), and particulate ammonium nitrate has been associated with the deterioration of atmospheric visibility (White and Roberts, 1977). The development of strategies to reduce such impacts requires measurements of ambient air quality to guide the formulation of rates of formation and removal to observe the response due to changes in N-oxides emissions. The sampling of HNO_3 and particulate nitrate salts is difficult because of possible biases due to the shifts in the equilibria of the dry and wet HNO_3–NH_3–NH_4NO_3 systems. The equilibrium thermodynamics of these systems are known (Stelson *et al.*, 1979; Stelson *et al.*, 1984) but the evaporation kinetics are not. Such shifts may be induced in the sampler by changes in air temperature or HNO_3, NH_3, or water vapor concentrations, but the response time cannot be easily predicted due to the lack of kinetic data for evaporation from dry and wet particles.

A convenient active technique to separate reactive trace gas from suspended particles with diameter $> 0.01\ \mu m$ is to flow the aerosol through a conduit whose wall is a perfect sink for the gas (Browning and Ackley, 1962; Bennett and Adams, 1968; Smith *et al.*, 1969; Durham *et al.*, 1978). The technique takes advantage of the relatively large diffusion coefficients of reactive trace gases compared to particles. For a tube with laminar flow, Gormley and Kennedy (1949) have reported the mass penetration equation for species diffusion to a 'perfect-sink' wall (first term only):

$$C/C(0) = \alpha \exp(-11.49\,Dx/Q) \qquad (1)$$

where $C(0)$ = concentration of trace reactive gas at inlet, $\mu g\ m^{-3}$
$\alpha = 0.819$
D = mutual diffusion coefficient, $cm^2\ s^{-1}$
Q = volume flow rate, $cm^3\ s^{-1}$
C = average concentration of trace reactive gas at x, $\mu g\ m^{-3}$
x = axial distance from reactive tube inlet, cm.

The diffusion coefficients of reactive gases may be determined by fitting mass penetration data to Equation (1) (Thomas, 1955; Bennett and Adams, 1968; Durham and Fish, 1971). If the diffusion coefficient of the trace reactive gas in air is known, then 'perfect-sink' conduits may be designed and operated as ambient air samplers to deplete a predictable fraction of the gas. $C(0)$ may be determined by measuring the quantity of gas that deposited to a fraction or penetrated a conduit with a 'perfect-sink' wall.

Passive samplers based on Fickian diffusion may be designed to collect trace reactive gases in the presence of particles. A convenient design consists of a stagnant tube with an inert inner wall, an open end (or an inert, permeable membrane cap), and an end cap whose inner surface is a 'perfect sink' for the trace gas (Coutant and Scott, 1982). The average ambient concentration of the reactive trace gas is given by

$$C(0) = (mL)/(AtD) \qquad (2)$$

where $C(0)$ = the average concentration at the open end, $\mu g\ m^{-3}$
m = mass of reactive trace gas accumulated by the end cap, μg
L = the axial length of the inert tube, cm
A = tube's cross-sectional area, cm^2
t = sampling duration, s.

A common variable to the active and passive samplers is their dependence on the mutual reactive gas–air molecular diffusion coefficient. If D is altered during the sampling period and is not accurately known, a bias is introduced into the determination of $C(0)$. Slight variations to D during sampling may result from temperature and pressure changes. However, if the reactive trace gas forms molecular complexes (e.g. dimers, hydrates), then the performance of diffusion-based samplers will be substantially altered due to the decrease of the diffusion coefficient.

It has been reported that the HNO_3–air diffusion coefficient decreases (from 0.12 to 0.05 $cm^2 s^{-1}$) as a function of relative humidity (0–95%) and suggested that the likely cause is the formation of the hydrates $HNO_3 \cdot nH_2O$ (Braman *et al.*, 1982; Eatough *et al.*, 1985). For a typical diffusion-depletion tube 50 cm long and operated in laminar flow at 16.7 $cm^3 s^{-1}$, the penetration of HNO_3 as the postulated hydrates would increase from 1.6 to 17.8% as relative humidity increased from 0 to 95%. If such modifications of the effective HNO_3–air diffusion coefficients are not taken into account (e.g. sampling at constant relative humidity), then the change in penetration transmits a bias to the estimate of HNO_3 concentration. The response of a passive sampler of the type described above is greater, as the collected mass is directly proportional to D. Since Eatough *et al.* (1985) have interpreted results reported by Durham and Spiller (1982) to support the existence of gaseous hydrates of HNO_3, we have re-examined the dependence of the HNO_3–air diffusion coefficient as a function of relative humidity.

METHOD

Theory

The fractional penetration of a trace reactive gas being removed by diffusion to a 'perfect-sink' wall is given by Equation (1), which requires: (a) a well-developed laminar flow in the tube, (b) that the gas not be generated in the tube or depleted except at the wall, and (c) that $C/C(0) < 0.819$, since the series solution has been truncated. D may be determined from Equation (1) by regressing measurements of $C/C(0)$ and x at constant Q. For a reactive wall that accumulates the trace gas, direct measurements of $C/C(0)$ are not practical, but $C/C(0)$ can be obtained from the measurements of the deposited mass (M_j) along discrete sections of the tube. The cumulative deposit of mass (F_i) through i discrete section is:

$$F_i = \sum_1^i M_j \tag{3}$$

$$= M_T(1 - C/C(0)) \tag{4}$$

$$= M_T[1 - \alpha \exp(-11.49\, Dx/Q)] \tag{5}$$

where M_T = total mass of trace reactive gas entering tube, and x corresponds to the end point of M_i. If the discrete sections are of uniform length Δx, then Equation (5) may be expressed as

$$F_i = M_T[1 - \alpha \exp(11.49\, Di\Delta x/Q)] \tag{6}$$

where $\Delta x = x/i$.

The mass of the reactive trace gas deposited on section j is

$$M_{j=i} = (F_i - F_{i-1}),\ i > 1 \tag{7}$$

$$= K \exp(-11.49\, Dx/Q) \tag{8}$$

where

$$K = \alpha M_T[-1 + \exp(11.49\, D\Delta x/Q)]. \tag{9}$$

Then,

$$\ln(M_j) = \ln(K) - 11.49\, Dx/Q. \tag{10}$$

Equation (10) is the differential form of Equation (1). It carries the condition that $i > 1$ which, in addition to the truncation problem previously mentioned, excludes the first section (M_1) from the regression of ln M_j against x to obtain estimates of D and M_T. The precision of the measurement of the mass on the sections usually decreases as mass decreases. Therefore, ln M_j must be weighted by the variance (Bevington, 1969) to remove the improper influence of the more imprecise measurements. The weighting factor is:

$$W_j = (M_j/s_j)^2;\ s = \text{standard deviation.} \tag{11}$$

If M_T is known, then Equation (10) may be expressed as

$$\ln(M_j/M_T) = \ln > (K/M_T) - 11.49\, Dx/Q, \tag{12}$$

and the regression determines the value of α, which has a theoretical value of 0.819 (Gormley and Kennedy, 1949).

EXPERIMENTAL

The deposition patterns of HNO_3 were measured in inert Teflon pipes (i.d. $\cong$ 0.9 cm) 94 cm long lined with nylon fiber mats (thickness = 0.015 cm). Since well-developed laminar flow is a necessary condition at the entrance to the reactive zone, a 47-cm bare section of Teflon was left ahead of the reactive nylon zone. Also, a 7-cm bare section of Teflon was left downstream to prevent disturbance of the flow exiting the nylon zone. A nylon filter in a Teflon holder trapped the HNO_3 that penetrated the tube. The gaseous HNO_3 was generated by three different methods depending on the relative humidity required. For the lowest relative humidity, ~5% r.h., HNO_3 was generated by vaporizing 0.05 ml of 0.1 N HNO_3 with air from an Aadco clean air system. For the intermediate relative humidities, 30 and 40%, HNO_3 was generated by vaporizing 0.05 ml of 0.1 N HNO_3 with filtered (glass fiber and nylon filters) room air. For the highest relative humidity, ~95% r.h., HNO_3 was generated by bubbling air from the clean air system through aqueous 1 M H_2SO_4 with a small amount of concentrated HNO_3. This HNO_3 contaminated air was pumped through the tubes at an approximate flow rate of 1000 $cm^3 min^{-1}$, regulated by a Precision Flow Devices Model 101 mass flow controller (standard deviation > 2%). After sampling, the nylon liner was cut into 8 sections, each 5.00 ± 0.05 cm long. The NO_3^- background was 0.01 μg per section. The sections and the filter were each extracted in 10 cm^3 of an aqueous solution of 0.003 M $NaHCO_3$ and 0.0024 M Na_2CO_3, which was also the carrier solution for the ion chromatograph. The standard deviation for determining the NO_3^- mass in the extract was the larger of 0.3 μg or ±3%. The analytical errors dominated those due to flow rate fluctuations and sectioning the nylon liner.

RESULTS

The laboratory conditions for each of the seven experiments are given in Table 1. These experiments are paired replicates for temperature, pressure, and relative humidity, except for No. 5, whose replicate was lost due to malfunction of the ion chromatograph. For each experiment, the weighted values of ln (M_j/M_T) were regressed against the axial distance x to estimate ln (K/M_T) and $-11.49\ (D/Q)$, which are the intercept and slope, respectively, of Equation (12). The estimates of these parameters are in Table 2. The weighted reduced chi-square ($\chi^2_\nu = \chi^2/\nu$) for each

Table 1. Experimental conditions

Exp. No.	Total NO_3^- (μg)	Flow rate ($cm^3 s^{-1}$)	Temperature (°C)	Pressure (atm)	Rel. humidity (%)
1	74.8 ± 3.9	16.00 ± 0.32	23.5 ± 0.2	1.005	95 ± 5
2	88.4 ± 4.2	17.17 ± 0.34	23.5 ± 0.2	1.005	95 ± 5
3	142.8 ± 6.2	17.17 ± 0.34	22.8 ± 0.2	0.993	40 ± 5
4	113.8 ± 5.1	16.00 ± 0.32	22.8 ± 0.2	0.993	40 ± 5
5	226.8 ± 9.6	17.17 ± 0.34	23.3 ± 0.2	1.000	30 ± 5
6	171.0 ± 7.3	17.17 ± 0.34	23.9 ± 0.2	1.002	5 ± 5
7	166.6 ± 6.7	16.00 ± 0.32	23.9 ± 0.2	1.002	5 ± 5

Table 2. Estimates of parameters to fit Equation (12)

Exp. No.	Intercept = ln (K/M_T)	Slope = $-11.49\ D/Q$ (cm^{-1})	χ^2_ν	ν	$P_x(\chi^2, \nu)$ (%)*
1	−0.759 ± 0.056	−0.0904 ± 0.0035	0.0709	5	>99
2	−0.828 ± 0.048	−0.0834 ± 0.0028	0.8674	5	50
3	−0.996 ± 0.040	−0.0760 ± 0.0020	1.3283	5	25
4	−0.892 ± 0.044	−0.0811 ± 0.0024	0.5184	5	76
5	−0.905 ± 0.036	−0.0794 ± 0.0016	2.2617	5	5
6	−0.812 ± 0.040	−0.0843 ± 0.0020	1.6802	5	13
7	−0.916 ± 0.039	−0.0780 ± 0.0019	1.5997	5	16

*Probability of exceeding χ^2_ν.

experiment was calculated from (Bevington, 1969):

$$\chi^2_\nu = (1/\nu)\left\{\sum_1^8 W_j[\ln(M_j/M_T) - \ln(\hat{M}_j/M_T)]^2\right\} \quad (13)$$

$$= (1/\nu)\left\{\sum_1^8 W_j[\ln mj - \ln \hat{M}_j]\right\}$$

where $\ln \hat{M}_j$ is estimated from the regression equation with the parameters in Table 1, and ν is the degree of freedom (number of data points − number of coefficients estimated − 1). Except for Experiment No. 1, the values of the reduced chi-squares are contained within the 95% confidence interval, which is $0.1662 < P_x(\chi^2, \nu) < 2.5000$. The reduced chi-square is also equal to the ratio of the variance of the fit to the variance of the data. If the two uncertainties are equal, the reduced chi-square should be approximately unity. The reduced chi-square for Experiment No. 1 is much less than unity; that may be due to an overestimate of the experimental error or fortuitous fluctuations in the variance of the fit.

Estimates of α were made from the intercepts $\ln(K/M_T)$ in Table 2 through Equation (12). The standard deviations of α were obtained by the transformation (Bevington, 1969):

$$s_\alpha = s \ln(K/M_T)\, d[\ln(K/M_T)]/d(K/M_T) \quad (14)$$

$$= s \ln(K/M_T)\{[(K/M_T)$$

$$\exp(K/M_T)]/\exp(57.45\, D/Q) - 1]\}.$$

The estimates of $\alpha \pm s$ for each experiment are given in Table 3. The variance-weighted average $\bar{\alpha} \pm \bar{s} = 0.829 \pm 0.012$, which agrees well with the theoretical value of 0.819 derived by Gormley and Kennedy (1949).

Table 3. Estimates of α and D_0 from fit to Equation (12)

Exp. No.	D_0 ($cm^2 s^{-1}$)	α
1	0.128 ± 0.005	0.818 ± 0.035
2	0.126 ± 0.004	0.844 ± 0.034
3	0.114 ± 0.003	0.799 ± 0.032
4	0.113 ± 0.003	0.819 ± 0.032
5	0.120 ± 0.002	0.830 ± 0.027
6	0.127 ± 0.003	0.846 ± 0.028
7	0.109 ± 0.003	0.838 ± 0.030
Weighted average	0.118 ± 0.003	0.829 ± 0.012

The estimates of D have been made from the slopes in Table 2 and scaled to the reference condition $T = 298$ K and $P = 1$ atm by

$$D_0 = P(298/T)^{1.5} D. \quad (15)$$

The variance-weighted average $\bar{D}_0 \pm \bar{s} = 0.118 \pm 0.003\ cm^2 s^{-1}$.

For each experiment, the fraction mass deposited is plotted as a function of γ, where

$$\gamma = 11.49\,(1/Q)(T/298)^{1.5}(1/P)x. \quad (16)$$

The γ-coordinate normalizes each point to the reference temperature (298 K), pressure (1/atm), and flow rate of 1 $cm^3 s^{-1}$, and Equation (12) becomes

$$\ln(M/M_T) = \ln(K/M_T) - D_0\gamma. \quad (17)$$

The regression curve with the weighted averages of α

$= 0.829$ and $D_0 = 0.118\ cm^2\ s^{-1}$ is line B in Fig. 1. For $\gamma \cong 3.5$, 7 and 10, the seven points cannot be resolved until γ increases.

The cluster of seven points at A in Fig. 1 corresponds to an average mass percent of 45.6 ± 1.0 at $\gamma = 3.4 \pm 0.1\ cm^{-2}\ s$. Thus, the fraction of mass deposited on the first section is constant and reproducible for the relative humidity range 5–95%.

DISCUSSION

The excellent fit of the HNO_3 deposition data to Equation (12) and the constant values of α and D over the relative humidity range 5–95% indicates that the nylon-lined tube satisfies the Gormley–Kennedy condition that the wall be a 'perfect sink.' The values of α and D exhibit no dependence on relative humidity.

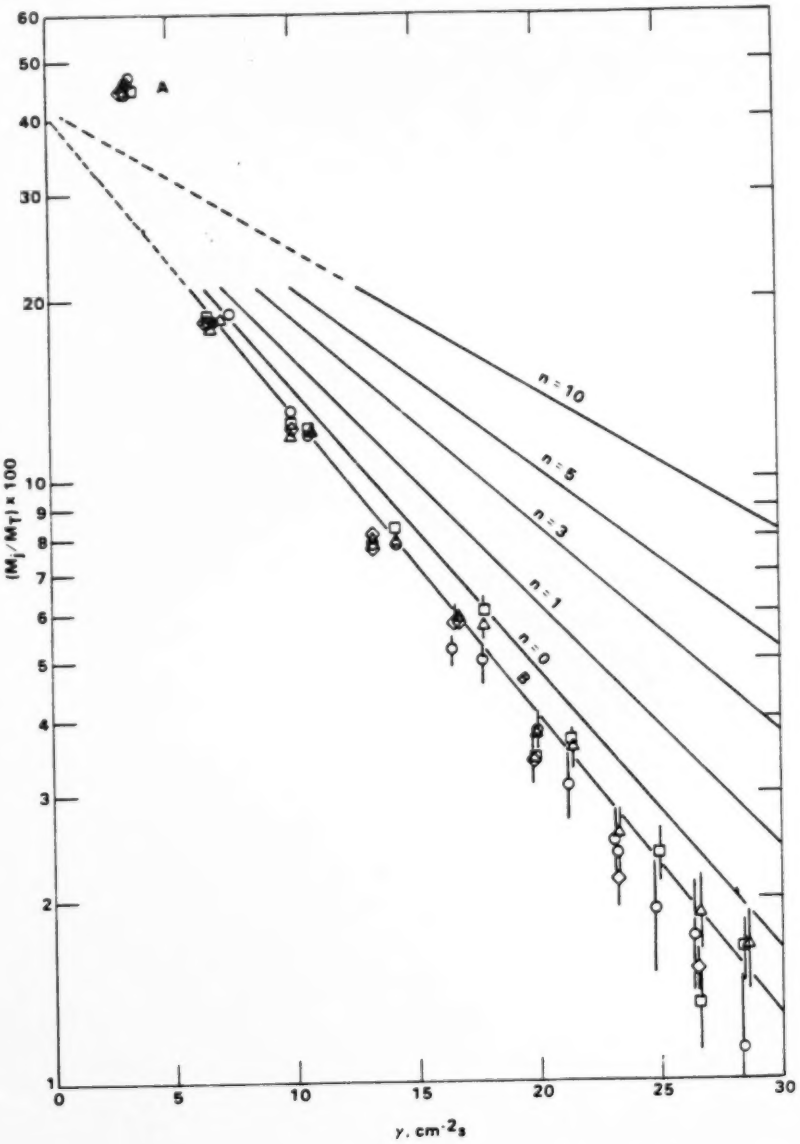


Fig. 1. Percent mass deposited to discrete section ($\Delta x = 5$ cm) vs γ. For example, the seven points clustered at A represent the percent mass deposited to the first 5-cm section and are plotted at the section's exit coordinate ($x = 5$ cm corresponds to $\gamma = 3.4 \pm 0.1\ cm^{-2}\ s$). In γ-coordinates, the plotted lines have slopes of $-D_0$. Line B is the regression line calculated for the data points and has the weighted γ and D_0 values contained in Table 3. The estimate of standard deviation for each point is shown as a vertical line or is less than the dimension of the point, which is the case for $\gamma < 15\ cm^{-2}\ s$. The lines indicated by $n = 0$, 1, 3, 5 and 10 have D_0s calculated for the hydrates $HNO_3 \cdot nH_2O$.

That is, the deposition of HNO_3 to the nylon is controlled solely by gaseous diffusion; there is no exhibited surface resistance, indicating that possible surface water films do not reduce nylon's reactivity. Also, HNO_3 vapor did not change its diffusion coefficient as a function of relative humidity in the range 5–95%; this observation agrees with Eatough *et al.* (1985).

The diffusion coefficients for $HNO_3 \cdot nH_2O$ were calculated from Gilliland's (1934) semi-empirical equation and the predicted deposition profiles are plotted in Fig. 1 for $n = 0$, 1, 3, 5 and 10. The calculated value of $0.113\ cm^2\ s^{-1}$ for $n = 0$ corresponds well to our experimental value of $0.118 \pm 0.003\ cm^2\ s^{-1}$, and it agrees well with the value n of $0.103\ cm^2\ s^{-1}$ reported by Eatough *et al.* (1985) and $0.121\ m^2\ s^{-1}$ (not referred to standard T and P) for low relative humidity reported by Braman *et al.* (1982). Eatough *et al.* (1985) observed that D_0 determined in tungstic acid-lined tubes decreased as a function of relative humidity. Although Braman *et al.* (1982) and Eatough *et al.* (1985) did not present experimental determinations of α as evidence that their sampling tubes satisfied the Gormley–Kennedy (1949) conditions, it is likely that the tungstic acid surface was not a 'perfect sink' due to exceeding surface capacity or influences of absorbed water.

Our results demonstrate that gaseous HNO_3 does not change hydration number over the relative humidity range 5–95%; comparison with Gilliland's semi-empirical theory suggests that HNO_3 is not hydrated for that range of relative humidity. Eatough *et al.* (1985) report thermodynamic calculations that indicate n varies from 0.8 to 1.2 for relative humidity from 5 to 95%. However, the hydration number of HNO_3 can be established unequivocally only by examining the i.r. spectra of HNO_3 as a function of relative humidity. We are not aware of such a study, but Tuazon *et al.* (1978, 1981) have observed in the Los Angeles atmosphere ν_5 ($= 879\ cm^{-1}$, the ONO angle deformation) and $2\nu_9$ ($= 896\ cm^{-1}$, the overtone of the HO torsion). These reported frequencies are not shifted with respect to reference spectra of the pure vapor, which has been reported by McGraw *et al.* (1965). FTIR (ν_5, $2\nu_9$) was included in an intercomparison study of HNO_3 measurement methods. For 12 selected sample periods, FTIR demonstrated good correspondence with the median HNO_3 concentrations determined from all the methods (Spicer *et al.*, 1982). Thus, for these periods, it is unlikely that HNO_3 was hydrated; otherwise, ν_5 and $2\nu_9$ would have been shifted and not observed.

CONCLUSIONS

The diffusion coefficient of HNO_3 in air ($T = 298$ K, $P = 1$ atm) is $0.118 \pm 0.003\ cm^2\ s^{-1}$. No influence of relative humidity (5–95%) was exhibited.

REFERENCES

Bennett R. L. and Adams R. E. (1968) Development of a sampling device for distinguishing the forms of iodine in a humid atmosphere. *Proc. 10th AEC Air Cleaning Conf.* (CONF-680821), New York, 28 August, 1968 pp. 235–262.

Bevington P. R. (1969) *Data Reduction and Error Analysis for the Physical Sciences.* McGraw-Hill, New York.

Braman R. S., Shelley T. J. and McClenney W. A. (1982) Tungstic acid for preconcentration and determination of gaseous and particulate ammonia and nitric acid in ambient air. *Analyt. Chem.* **54**, 358–364.

Browning W. E., Jr. and Ackley R. D. (1962) Characterization of millimicron radioactive aerosols and their removal from gases. U.S. Atomic Energy Commission TID-7641, pp. 130–147.

Coutant R. W. and Scott D. R. (1982) Applicability of passive dosimeters for ambient air monitoring of toxic organic compounds. *Envir. Sci. Technol.* **16**, 410–413.

Durham J. L. and Fish B. R. (1971) Diffusion coefficient of SO_2 in air. *Envir. Lett.* **2**, 13–21.

Durham J. L. and Spiller L. L. (1982) Measurement of gaseous, volatile and non-volatile inorganic nitrate in Riverside, California. *Proc. of Div. of Envir. Chem. 184th National ACS Meeting*, Kansas City, Missouri.

Durham J. L., Wilson W. E. and Bailey E. B. (1978) Application of an SO_2 denuder for continuous measurement of sulfur in submicrometric aerosols. *Atmospheric Environment* **12**, 833–886.

Eatough D. J., White V. F., Hansen L. D., Eatough N. L. and Ellis E. D. (1985) Hydration of nitric acid and its collection in the atmosphere by diffusion denuders. *Analyt. Chem.* **57**, 743–8.

Gilliland E. R. (1934) Diffusion coefficients in gaseous systems. *Ind. Engng Chem.* **26**, 681–685.

Gormley P. G. and Kennedy M. (1949) Diffusion from a stream flowing through a cylindrical tube. *Proc. R. Irish Acad., Sec A* **52**, 163–9.

Likens G. E., Bormann F. H., Pierce R. S., Eaton J. S. and Johnson N. M. (1977) *Biogeochemistry of a Forested Ecosystem.* Springer, New York.

McGraw G. E., Bernitt D. L. and Hisatsune I. C. (1965) Vibrational spectra of isotopic nitric acids. *J. Chem. Phys.* **42**, 237–244.

Smith B., Watman J. and Fish B. (1969) Interactions of airborne particles with gases. *Envir. Sci. Technol.* **3**, 558–562.

Spicer C. W., Howes J. E., Jr., Bishop T. A., Arnold L. H. and Stevens R. K. (1982) Nitric acid measurement methods: an intercomparison. *Atmospheric Environment* **16**, 1487–1500.

Stelson A. W., Bassett M. E. and Seinfeld J. H. (1984) Thermodynamic equilibrium properties of aqueous solutions of nitrate, sulfate and ammonium. In *Chemistry of Particles, Fogs, and Rain* (edited by Durham J. L.), pp. 1–52. Butterworth, Boston, MA.

Stelson A. W., Friedlander S. K. and Seinfeld J. H. (1979) A note on the equilibrium relationship between ammonia and nitric acid and particulate ammonium nitrate. *Atmospheric Environment* **13**, 369–371.

Thomas J. W. (1955) The diffusion battery method for aerosol particle size determination. *J. Colloid Sci.* **10**, 246–255.

Tuazon E. C., Graham R. A., Winer A. M., Easton R. R., Pitts J. N., Jr. and Hanst P. L. (1978) A kilometer pathlength Fourier transform infrared system for the study of trace pollutants in ambient and synthetic atmospheres. *Atmospheric Environment* **12**, 865–875.

Tuazon E. C., Winer A. M. and Pitts J. N., Jr. (1981) Trace pollutant concentrations in a multiday smog episode in the California South Coast Air Basin by long path length Fourier transform infrared spectroscopy. *Envir. Sci. Technol.* **15**, 1232–1237.

White W. H. and Roberts P. T. (1977) On the nature and origins of visibility reducing species in the Los Angeles Basin. *Atmospheric Environment* **11**, 803–812.

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This article documents research that was conducted under the auspices of the U.S. Environmental Protection Agency (USEPA). As an arm of the government, the USEPA has a paid up, non-exclusive, irrevocable, worldwide license to reproduce, prepare derivative works, and distribute to the public all of the material contained herein, and to grant others acting on its behalf the right to do so. The USEPA grants to the National Technical Information Service, Department of Commerce, the right to act as its agent in the distribution of this material.